

## Bonding in 1,2,3-Triazoles. II. The Crystal Structures of 1-Phenyl-3-methyl- and 1-Methyl-3-phenyl-4-(1,2,3-triazolio)sulfide

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The crystal structures of the title compounds,  $C_9H_9N_3S$ , have been determined by X-ray diffraction techniques. The first compound is triclinic, space group  $P\bar{1}$ , with  $a=11.08(3)$  Å,  $b=7.69(2)$  Å,  $c=6.00(2)$  Å,  $\alpha=97.5(2)^\circ$ ,  $\beta=105.4(2)^\circ$  and  $\gamma=106.3(2)^\circ$ . The crystals of the other compound are monoclinic and exist in two modifications, space group  $Cc$  with  $a=9.32(3)$  Å,  $b=11.72(2)$  Å,  $c=9.13(3)$  Å,  $\beta=107.1(5)^\circ$ , and space group  $P2_1/a$  with  $a=17.38(2)$  Å,  $b=7.26(3)$  Å,  $c=7.79(3)$  Å and  $\beta=104.9(5)^\circ$ . Three-dimensional data were collected using an automatic equi-inclination diffractometer and  $MoK\alpha$  radiation. The structures were refined by the method of least-squares to  $R$ -values of about 0.05. There are no significant differences between the geometries of the triazole rings in the three structures. The angle between the phenyl ring and the triazole ring is  $12.5^\circ$  for the 1-phenyl- and  $48.0^\circ$  and  $57.8^\circ$  for the two 3-phenyl substituted modifications. Atomic charges are estimated on the basis of semiempirical MO-calculations.

The structure of 1,3-dimethyl-4-(1,2,3-triazolio)sulfide has been determined previously<sup>1</sup> (part I of this series) in order to confirm the charge distribution indicated by photo electron<sup>2</sup> and  $^{13}C$  NMR spectra.<sup>3</sup> In continuation of this investigation the structure determinations of 1-phenyl-3-methyl- and 1-methyl-3-phenyl-4-(1,2,3-triazolio)sulfide\* were carried out. The  $^{13}C$  NMR data indicate an almost planar PMTS molecule, whereas the MPTS molecule has a large angle between the two rings.<sup>3</sup> In

\* Henceforth referred to as PMTS and MPTS, respectively. The two modifications of MPTS are designated MPTS-P and MPTS-C in accordance with their space group.

this respect the present investigation is part of an attempt to correlate  $^{13}C$  NMR data with molecular geometry.

### EXPERIMENTAL

The possible space groups were established from Weissenberg and precession photographs using Cu and Mo radiation. Three-dimensional data between a cylinder of radius  $\gamma=5.4^\circ$  and a hemisphere with  $\sin \theta/\lambda < 0.7 \text{ \AA}^{-1}$  were measured on an automatic equi-inclination diffractometer (Stoe & Cie, DBR) using graphite monochromatized  $MoK\alpha$  radiation. The dimensions of the crystals were approximately  $0.2 \times 0.2 \times 0.3$  mm. The reflections were corrected for Lorentz and polarization effects, but no correction for absorption was applied. The structure analyses were performed using Patterson and direct methods.<sup>4,5</sup> The calculations included full-matrix least-squares refinements of positional and anisotropic, respectively isotropic, thermal parameters for non-hydrogen and hydrogen atoms. The atomic scattering factors for C, N and S are those given by Cromer and Mann,<sup>6</sup> and for H, those given by Stewart *et al.*<sup>7</sup> The weights were of the form

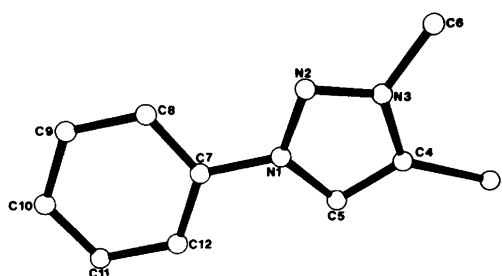


Fig. 1. PMTS viewed along the  $b^*$ -axis.

Table 1. Crystal data. C<sub>9</sub>H<sub>9</sub>N<sub>3</sub>S, *M* = 191.3, μ(MoKα) = 2.8 cm<sup>-1</sup>.

	PMTS	MPTS-C	MPTS-P
Crystal system	triclinic	monoclinic	monoclinic
Melting point (°C)	193–194	110–112	100–102
<i>V</i> / <i>Z</i> Å <sup>3</sup>	230.7	238.3	237.5
<i>a</i> (Å)	11.08(3)	9.32(3)	17.38(2)
<i>b</i> (Å)	7.69(2)	11.72(2)	7.26(3)
<i>c</i> (Å)	6.00(2)	9.13(3)	7.79(3)
α(°)	97.5(2)		
β(°)	105.4(2)	107.1(5)	104.9(5)
γ(°)	106.3(2)		
Space group	P1̄ (No. 2)	Cc (No. 9)	P2 <sub>1</sub> /a (No. 14)
<i>D</i> <sub>c</sub> (g/cm <sup>3</sup> )	1.38	1.33	1.34
<i>Z</i>	2	4	4
Total number of reflections	4566	2162	4338
Number of independent observations ( <i>I</i> > 2σ( <i>I</i> ))	1663	883	1332
$R = \frac{\sum   F_o  -  F_c  }{\sum  F_o }$	0.051	0.039	0.039
$R_w = \left( \frac{\sum w( F_o  -  F_c )^2}{\sum w F_o ^2} \right)^{\frac{1}{2}}$	0.066	0.038	0.047

Table 2. Final atomic coordinates × 10<sup>4</sup>. The estimated standard deviations × 10<sup>4</sup> are given in parentheses. The values of the hydrogen atoms are multiplied by 10<sup>3</sup>.

Atom	PMTS			MPTS-C			MPTS-P		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
S	-1304(1)	6356(1)	2307(1)	2544(0)	2349(1)	-0120(0)	4438(1)	8877(1)	7666(1)
N1	2496(2)	7487(3)	4997(4)	-1260(4)	0814(3)	-0737(4)	4243(1)	6173(3)	3279(2)
N2	2264(2)	8278(3)	6852(4)	-0762(3)	0681(3)	0756(4)	3745(1)	5185(3)	3913(2)
N3	0959(2)	7947(3)	6074(4)	0595(4)	1178(2)	1114(3)	3757(1)	6038(3)	5456(2)
C4	0347(2)	6971(3)	3764(4)	0962(4)	1617(3)	-0141(4)	4256(2)	7545(3)	5806(3)
C5	1391(2)	6689(4)	3090(5)	-0298(5)	1342(3)	-1319(4)	4562(2)	7588(3)	4318(3)
C6	0328(3)	8561(5)	7719(6)	-2763(6)	0396(5)	-1568(7)	4368(2)	5675(5)	1538(4)
C7	3829(2)	7540(4)	5170(5)	1435(4)	1252(3)	2706(4)	3252(2)	5328(3)	6500(3)
C8	4766(3)	8058(6)	7373(7)	2923(5)	0968(3)	3189(5)	2682(2)	6466(4)	6889(3)
C9	6050(3)	8092(7)	7533(8)	3703(5)	1056(4)	4730(5)	2183(2)	5752(5)	7852(4)
C10	6361(3)	7573(5)	5551(7)	2992(6)	1420(4)	5759(5)	2272(2)	3957(5)	8439(4)
C11	5414(3)	7038(6)	3400(7)	1509(6)	1713(4)	5266(5)	2836(2)	2839(4)	8036(4)
C12	4132(3)	7036(6)	3191(6)	0686(5)	1634(4)	3720(4)	3338(2)	3512(4)	7051(3)
H1	137(3)	605(4)	151(6)	-053(4)	147(4)	-234(5)	493(2)	844(4)	403(4)
H2	-038(6)	770(8)	748(11)	-283(8)	-036(9)	-144(9)	465(3)	662(7)	114(6)
H3	018(6)	957(8)	765(10)	-346(7)	070(6)	-122(7)	388(3)	564(6)	071(6)
H4	097(5)	893(7)	932(10)	-287(7)	062(6)	-247(8)	467(3)	462(7)	164(6)
H5	452(4)	838(6)	900(8)	340(3)	073(3)	252(4)	262(2)	767(5)	645(4)
H6	677(5)	849(7)	885(9)	479(6)	087(6)	503(5)	178(2)	661(6)	809(5)
H7	715(5)	746(6)	562(9)	362(5)	142(4)	687(5)	195(2)	353(5)	915(5)
H8	571(6)	665(8)	184(11)	078(6)	205(5)	590(7)	291(2)	158(5)	848(5)
H9	340(4)	658(6)	176(8)	-037(5)	185(4)	333(5)	375(2)	272(5)	674(4)

$w^{-1} = a + b|F_o| + c|F_o|^2 + d \sin \theta/\lambda$  with the coefficients adjusted to give as uniform a distribution of  $w|\Delta F|^2$  as possible.<sup>8</sup> For the illustrations the ORTEP II program<sup>9</sup> was used. Crystal data and *R*-values are listed in Table 1. The final positional parameters with standard deviations are listed in Table 2, and the labelling of the atoms are shown in Fig. 1. Lists of thermal parameters and observed and calculated structure factors may be obtained from the authors on request.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURES

Bond lengths and bond angles and their estimated standard deviations are listed in Tables 3 and 4. The three phenyl groups are all planar within experimental error. Analyses of the triazole rings (Table 5) show planar groups, which in PMTS includes the sulfur atom, whereas the methyl group is significantly out of plane. In the MPTS compounds, both the sulfur atom and the methyl group are significantly out of plane, in MPTS-C to the same side, and in MPTS-P to opposite sides of the

plane. The angles between the triazole rings and the phenyl rings are 12.5, 48.0 and 57.8° for PMTS, MPTS-C and MPTS-P, respectively. The angle between the two planes may in all three structures primarily be described as a rotation around the N-C7-C10 line, the angles between this line and the normals to the two planes ranging from 86.1 to 89.9°.

The thermal movements of the phenyl carbons, except C7, in PMTS are highly anisotropic with the largest amplitudes along the *b*\*-axis, which is almost normal to the phenyl ring. In the two other compounds no such distinct anisotropy along the normal to the phenyl ring is found.

The deviation from 120° of the endocyclic angles in the phenyl rings largely follows the trends found for substitution of highly electronegative groups on benzene (*cf.* Norrestam and Schepper<sup>10,11</sup>). At the *ipso* position the deformation is 1.1° in PMTS and 1.7 and 2.1° for the C- and P-form of MPTS, respectively. However, only the deformations in MPTS-P possess 2-fold symmetry around the C7-C10 line. This deviation from 2-fold symmetry may possibly be related to the shorter intra-

Table 3. Bond distances (Å) with estimated standard deviations.

Atoms	PMTS Distance	Atoms	MPTS-C Distance	MPTS-P Distance
S-C4	1.699(5)	S-C4	1.701(5)	1.700(5)
C4-C5	1.384(5)	C4-C5	1.377(10)	1.391(6)
C5-N1	1.354(4)	C5-N1	1.323(7)	1.335(5)
N1-N2	1.318(5)	N1-N2	1.314(7)	1.311(4)
N2-N3	1.332(5)	N2-N3	1.344(6)	1.346(4)
N3-C4	1.374(5)	N3-C4	1.387(6)	1.377(4)
N3-C6	1.455(6)	N1-C6	1.468(9)	1.470(5)
N1-C7	1.442(5)	N3-C7	1.437(9)	1.433(6)
C7-C8	1.373(6)	C7-C8	1.368(8)	1.378(5)
C8-C9	1.393(7)	C8-C9	1.385(9)	1.381(6)
C9-C10	1.365(8)	C9-C10	1.368(9)	1.377(6)
C10-C11	1.355(6)	C10-C11	1.366(9)	1.366(6)
C11-C12	1.392(7)	C11-C12	1.397(9)	1.386(7)
C12-C7	1.356(6)	C12-C7	1.387(8)	1.382(5)
C5-H1	1.00(3)	C5-H1	0.91(5)	0.96(3)
C6-H2	0.84(6)	C6-H2	0.90(11)	0.94(5)
C6-H3	0.84(7)	C6-H3	0.88(8)	0.92(4)
C6-H4	0.98(5)	C6-H4	0.84(8)	0.92(5)
C8-H5	1.10(5)	C8-H5	0.90(4)	0.94(3)
C9-H6	0.91(5)	C9-H6	1.00(5)	0.99(4)
C10-H7	0.89(6)	C10-H7	1.01(4)	0.94(4)
C11-H8	1.11(7)	C11-H8	1.09(7)	0.98(4)
C12-H9	0.96(4)	C12-H9	0.98(4)	0.99(4)

Table 4. Bond angles ( $^{\circ}$ ) with estimated standard deviations.

Atoms	PMTS Angle	Atoms	MPTS-C Angle	MPTS-P Angle
S-C4-C5	132.7(3)	S-C4-C5	131.7(2)	132.0(2)
S-C4-N3	124.7(2)	S-C4-N3	126.9(2)	126.1(2)
N3-C4-C5	102.6(3)	N3-C4-C5	101.4(4)	101.9(2)
C4-C5-N1	106.7(3)	C4-C5-N1	108.7(4)	107.5(3)
C5-N1-N2	113.2(3)	C5-N1-N2	113.4(3)	113.7(3)
N1-N2-N3	103.0(2)	N1-N2-N3	102.8(3)	102.9(2)
N2-N3-C4	114.4(3)	N2-N3-C4	113.8(3)	114.0(2)
N2-N3-C6	118.5(3)	N2-N1-C6	119.3(4)	118.6(2)
C4-N3-C6	127.0(3)	C5-N1-C6	127.3(4)	127.7(3)
C5-N1-C7	127.4(3)	C4-N3-C7	128.3(3)	128.0(2)
N2-N1-C7	119.4(2)	N2-N3-C7	117.8(3)	117.9(2)
N1-C7-C12	120.1(3)	N3-C7-C12	117.6(4)	119.1(2)
N1-C7-C8	118.7(3)	N3-C7-C8	120.7(4)	118.8(3)
C12-C7-C8	121.1(4)	C12-C7-C8	121.7(4)	122.1(3)
C7-C8-C9	118.5(4)	C7-C8-C9	119.3(4)	118.4(3)
C8-C9-C10	120.7(4)	C8-C9-C10	120.3(4)	120.3(3)
C9-C10-C11	119.7(4)	C9-C10-C11	120.0(4)	120.8(3)
C10-C11-C12	120.6(4)	C10-C11-C12	121.2(5)	120.2(3)
C11-C12-C7	119.3(3)	C11-C12-C7	117.4(4)	118.3(3)

molecular non-bonded distances from the carbon atoms in the *orto* position to N2 and S. In MPTS-P the distances C8-S and C12-N2 are 3.42 Å and 2.97 Å, respectively, compared to the corresponding distances in MPTS-C of 3.35 Å and 2.87 Å. In PMTS the C8-N2 distance is 2.76 Å.

The charge distributions (atomic units) in the molecules as calculated within the CNDO frame<sup>12</sup> show no significant differences between the three phenyl groups. The charges on the carbon atoms

Table 5. Distances in Å of atoms from the least squares planes of triazole. Atoms marked with \* are those defining the planes. The estimated standard deviations of the atoms from the planes are 0.0022 Å for PMTS, 0.0038 Å for MPTS-C and 0.0029 Å for MPTS-P.

Atoms	PMTS	MPTS-C	MPTS-P
*N1	-0.003	0.005	0.003
*N2	0.002	-0.003	0.000
*N3	-0.001	0.001	-0.002
*C4	-0.001	0.002	0.003
*C5	0.002	-0.004	-0.004
S	-0.002	0.072	0.061
C6	-0.058	0.037	-0.036
C7	-0.016	0.079	-0.038
H1	0.023	-0.008	-0.008

are alternant with a value of 0.11 at the *ipso* position, which is in agreement with what would be expected from the angular deformations at C7. The differences in this deformation between the two isomers may be related to the only significant difference in charge in the triazole groups. In PMTS charges of 0.13 and 0.03 are found for N1 and N3, respectively, whereas the corresponding values for MPTS are 0.24 and -0.11. The charges at S and C4 were calculated to -0.54 and 0.22 for PMTS and -0.49 and 0.22 for MPTS, indicating that the C-S bond of 1.70 Å largely is a single bond. For the remaining atoms the calculated charges are C5: -0.13, -0.10 and N2: -0.11, -0.14 for PMTS and MPTS, respectively. The CNDO calculations also indicate that the molecules possess large dipole moments. A comparison of the geometry of the triazole rings in several 1,3-substituted 4-(1,2,3-triazolio)sulfides as well as a general discussion of substitution effects are dealt with in subsequent papers.<sup>13,14</sup>

The packing of PMTS (Fig. 2) is accomplished by a stacking of slightly tilted phenyl rings and an alternating stacking of sulfur atoms and triazole rings along the *b*-axis. This indicates an electrostatic interaction between the negatively charged sulfur atom and the positively charged triazole group. The contact distances from S to the atoms

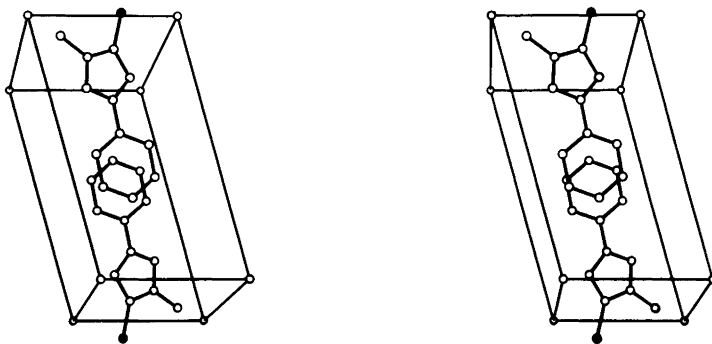


Fig. 2. Stereo view along the  $b^*$ -axis of the structure of PMTS. The sulfur atoms are shown as black spheres.

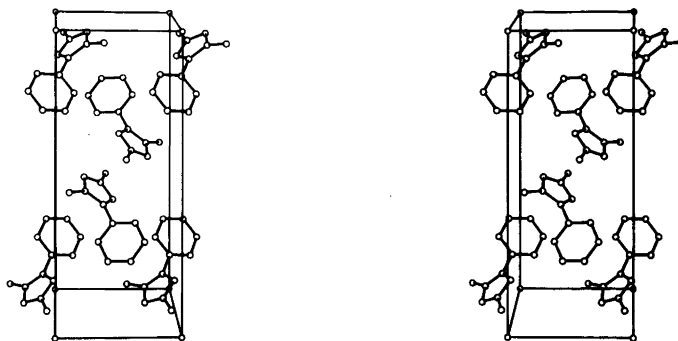


Fig. 3. Stereo view along the  $c^*$ -axis of the structure of MPTS-P.

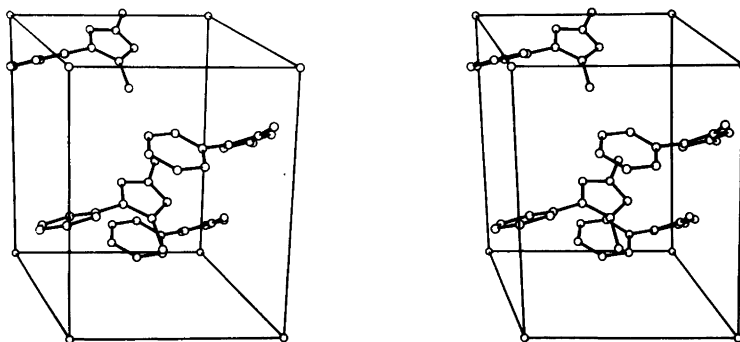


Fig. 4. Stereo view along the  $a^*$ -axis of the structure of MPTS-C.

in the triazole ring range from 3.56 Å for S-N2- $(\bar{x}, 1-y, 1-z)$  to 3.87 Å for S-C4 $(\bar{x}, 1-y, 1-z)$ . The other intermolecular distances are of the order expected from the corresponding van der Waals radii. The more efficient packing of PMTS is reflected in a smaller molar volume (231 Å<sup>3</sup>/molecule) than found for MPTS (238 Å<sup>3</sup>/molecule), and may account for the much higher melting point of PMTS. In both forms of MPTS the shorter intermolecular distances are found between a triazole ring and a phenyl ring (Figs. 3 and 4). In MPTS-P somewhat longer distances are found between triazole rings related by the center of symmetry. The shortest contacts from sulfur are in MPTS-C found to C12 $(1/2+x, 1/2-y, z-1/2)$  (3.60 Å) and in MPTS-P to C5 $(1-x, 2-y, 1-z)$  (3.65 Å).

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